A New Approach to measure Phonon Dispersion Relation (PDR) by Raman Scattering and a Downbending Observation in Diamond PDR

Shu-Lin Zhang,^a Lei Xia, Weihua Chen, D. Y. Li, Wanyu Li and Juan He

*State Key Laboratory for Artificial Microstructure and Mesoscopic Physics,
School of Physics, Peking University, Beijing 100871, China*

Abstract

The phonon dispersion relation (PDR), i.e., the dependence of phonon frequency ω on its wavevector q , $\omega(q)$, was measured traditionally by inelastic neutron scattering (INS) or inelastic X-ray scattering (IXS). A new approach to measure PDR by Raman scattering (RS) of nanostructures was proposed and applied to observe the longitudinal optical (LO) PDR of diamond successfully. Due to the higher resolution and accuracy of ω and q in RS, a clear downbending feature of ω with increasing q away from the Brillouin zone center was observed for the first time.

The validity of the new approach has been confirmed also by the appearing of the downward bending in PDR, which is originally measured by traditional high-resolution IXS experiment.

The downbending feature may give us a clue for deep understanding of the interactions occur in diamond, while the overbending feature observed by INS and IXS has been attributed to strong effective second-nearest-neighbor forces.

Keywords:

- A. Nanostructures;
- C. Diamond;
- D. Phonon dispersion relation;
- E. Raman spectroscopy.

1. Introduction

The phonon dispersion relation (PDR), $\omega(q)$, describes the dependence of the phonon frequency ω on its wavevector q and is an important foundation of solid state physics. The PDR is derived theoretically by the lattice dynamics and experimentally by the inelastic scattering (IS). For IS, the frequencies ω_i , ω_s , ω_q and the wavevectors $\mathbf{k}_i$, $\mathbf{k}_s$, $\mathbf{q}$ for the incident wave, scattered wave and phonon itself satisfy the conservation law of energy $E (= \hbar \omega)$ and momentum $\mathbf{P} (= \hbar \mathbf{k} \text{ or } \hbar \mathbf{q})$, i.e.,

$$\omega_i - \omega_s = \omega_q \quad (1)$$

^{a)}Electronic mail: slzhang@pku.edu.cn

$$\mathbf{k}_i - \mathbf{k}_s = \mathbf{q} \quad (2)$$

Thus, PDR can be derived by an IS. However, in the IS of light (i.e., Raman scattering, RS), there is a so-called Raman selection rule of $q = 0$, i.e., the phonons with $q \neq 0$ are Raman inactive [1]. As a result, the PDR is impossible to be deduced by RS and is traditionally measured by inelastic X-ray scattering (IXS) [2, 3] or inelastic neutron scattering (INS) [4, 5]. However, the IXS and INS is not as good as RS in terms of resolution, precision and accuracy of frequency. For example, the resolution, accuracy and precision of frequency are 64 cm^{-1} , 12 cm^{-1} and 2.5 cm^{-1} , respectively, even though for high resolution IXE [2]. In contrast, the resolution, accuracy and precision of frequency can easily reach to 0.2 cm^{-1} , 1.5 cm^{-1} and 0.25 cm^{-1} , respectively in RS. Therefore the PDR derived by RS should have an obvious advantage in resolution, precision and accuracy of frequencies and has hence attracted attention.

The RS spectra of nanostructures have been a subject since early 1980s and many significant theoretical, experimental and review articles [6-10] have been published in this field. It is well known that for nanostructures with a finite size must possess a finite size effect (FSE), by which one of the induced results is the loss of the translational symmetry and relaxation of the momentum $\mathbf{P}$ (i.e., wavevector k or q) conservation. That results in a consequence that the selection rule of phonon wavevector $q = 0$ in RS is relaxed and the wavevector of Raman active phonons can be non-zero, indicating a possibility to deduce PDR by RS.

It is well known that the uncertainty principle is a basic principle in quantum mechanics, which claims that the standard deviation of size L and wavevector q , ΔL and Δq , satisfies

$$\Delta L \Delta q \geq 1/2 \quad (3)$$

The uncertainty principle does not play an actual role in a macroscopic medium with large L . However, due to the value of L and corresponding ΔL of nanostructures being very small, the uncertainty principle may have a real impact in nanostructures. Thus, based on the uncertainty principle, the Δq of a nanostructure can be finite and the deduced value from by ΔL as well as the wavevector q of nanostructures with bulk wavevector q_b will be $q = q_b + \Delta q$. Since $q_b = 0$ as q_b being at the Brillouin zone center, we will have $q = \Delta q$ for nanostructures. That implies that q of nanostructures can be obtained by its ΔL directly. Moreover, if the relative standard deviation $\Delta L/L$ is smaller and equivalent for all of nanostructure samples being used, the dependence of ω on q for nanostructures can be deduced by various sizes of nanostructures. Additionally, if the crystal structure of nanostructures is the same as that of corresponding bulk material, the measured dependence of ω on q of the nanostructures can be considered as PDR. The above statement implies that a non-traditional approach to measure PDR by RS is valid.

In this paper the suggested non-traditional approach to measure PDR is confirmed by derivation of the longitudinal optical (LO) PDR of diamond by Raman spectra of nano-crystalline diamond (NCD).

2. Experimental methods

It has been mentioned that the nano-diamonds get smaller, the non-intrinsic structures and defects may appear [11, 12]. Therefore it is very important that the nano-diamond samples used to measure the PDR of diamond should be the diamond structure and have uniform size.

All samples named by NCD-U used in this work were prepared by a self-organization approach, of which NCD-U1 was prepared by the detonation method and NCD-U2-U5 were prepared by chemical vapor deposition. It is well known that the samples prepared by self-organization approach has a same crystalline structure with bulks and no impurity and distortion to be produced [13, 14]. Therefore the samples used are fitting the requirement of samples.

The transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images of samples were obtained from FEI Tecnai TEMF 30 and FEI Nano SEM 430, respectively. The transparent electron microscopy (TEM) images of NCD-U samples are shown in Fig 1. From visual inspection of the TEM image of over 100 clearly delineated particles of NCD-U, the average size L_{av} and standard deviation ΔL_{av} were obtained and listed in Table 1. The relative standard deviation $(\Delta L/L)_{av}$ of NCD-U samples has a similar value of 0.09 to 0.11, implying the nano-crystalline diamonds used have different but uniform sizes definitely.

The Raman spectral measurements were performed by using Renishaw Invia Raman microprobes in backscattering geometry at room temperature. The instrument resolution and spectral accuracy of the Raman microprobes are about 1.5 cm^{-1} and 0.5 cm^{-1} , respectively. In the treatment of measured Raman spectra, only the optical phonon with SP3 were used, which guarantees the PDR to belong to the optical phonon.

Besides, from Fig 1 we can also see that the NCD particles in samples have no shared orientation, indicating that the measured PDR can't be recognized to be along a certain principal axis. In this work we suppose that the measured PDR is along an average direction of the three principal axis, i.e., the Γ_L direction.

3. Results and discussion

The observed and fitted (with a Lorentzian line shape) Raman spectra excited by a 514.5 nm laser for samples NCD-U are shown in Fig 2 (a) in solid and dashed lines, respectively. From Fig 2 (a) we can see that the fitted spectra exhibit two peaks. It is

well known that the phonons of *LO* and *TO* of diamond degenerate at the Brillouin zoon center but split while leaving the center. Due to FSE the observed phonons of nanostructures could be away from the Brillouin zoon center, i.e., *LO* and *TO* phonons could be observed simultaneously. Thus we assign the two peaks to *TO* and *LO* phonons for the samples with size being smaller than 6.61 nm and *LO* and *D* phonons for a sample of the largest size, of which the *D* mode is originated from disorder structures in sample. The fitted RS frequencies, ω of *TO* and *LO*, were listed in Table 1. From Table 1 we can also see that the Raman frequency separation between *LO* and *TO* increases monotonously with decreasing of the sample size, conforming the sample possessing FSE and the measured RS spectra being definitely originated from NCD.

The wavevectors q were deduced from ΔL_{av} based on formula (3) and the corresponding reduced wavevectors q_r ($= q/q_{max}$; $q_{max} = \pi/a$, $a = 0.35668$ nm is the lattice constant of diamond) were listed Table 1

Based on the data in Table 1, the Raman frequencies of *LO* phonon ω_L with reduced wavevector q_r are drawn with solid triangle in Fig 3 (a). In Fig 3 (a), one can see a downward bending feature of ω_L with increasing of q_r just leaving the Brillouin zoon center. This feature is not found in the diamond PDR observed by traditional IXS [2, 3] and INS [4, 5] and thus may reflect that the present $\omega(q)$ derived by RS may not be reliability. To check the reliability we performed a comparison with independent RS experiments for UCD-U samples.

The first comparison is by using a single-size NCD sample. Such kind of samples quoted were the single NCD particles with size of 90 and 35 nm [15], for which we labeled them as NCD-S1 and NCD-S2, respectively. The sizes of NCD-S1 and NCD-S2 are just in between the sizes of NCD-1 (581.6nm) and NCD-2 (6.61nm). To deduce q we selected ΔL of NCD-S being $0.1 \times L$, as L is measured for a single particle and must possess a high accuracy. The ω_L of NCD-S with their reduced wavevectors q_r are listed in Table 1 and marked in Fig 3 (a) with red solid square. From Fig 3 (a), we can see clearly that the data of the NCD-S samples are located just between NCD-1 and NCD-2 in the down part of the downward bending, indicating the reliability of the downward bending feature and giving a positive confirmation on the PDR measured for NCD-U samples.

The second comparison is performed by a size-distributed NCD sample named as NCD-D. The SEM image of NCD-D is shown in Fig 1 (g) and the sizes of the NCD particles in NCD-D are 3-120 nm. The RS spectra of NCD-D were excited by 325, 488, 515, 633, 785 and 1064 nm lasers and shown in Fig 2 (b) in which the solid and dashed lines are the observed and fitted (with a Lorentzian) Raman spectra, respectively. The Raman frequencies, ω , of the fitted Raman peaks were listed in Table 2. Fig 2 (c) is the photo-luminescence (PL) spectrum of the NCD-D sample.

The PL spectrum indicates that the Raman spectra shown in Fig 2 (b) are indeed the resonant RS spectra. Thus, the size of nano-particles in NCD-D can be selected by the resonant size selection effect (RSSE) according to the wavelength λ_{ex} (i.e., excited energy E_{ex}) of the excitation lasers [16, 17].

For the selection of the nano-particle size L_{se} by RSSE, a dependence of sample size L on electron band gap energy, E_{gap} , is needed. For this requirement, a theoretical L dependence of E_{gap} for nano-diamond (ND) clusters showing in Fig 4 of Ref 18 was quoted. However, in Fig 4 of Ref 18, the E_{gap} range of 5.5-8.0 eV doesn't cover the energy range of the exciting laser λ_{ex} , 1.211-3.815 eV. Thus, it is impossible to select out the size of ND particles, L_{ex} , in NCD-D, directly from using Fig 4 of Ref 18. To overcome this difficulty, firstly, we figured out an average gradient G of the change of L with E_{gap} in the range of small E_{gap} in Fig 4^[18], obtaining $G = 1.556 \text{ nm/eV}$. Secondly, we found a fiducial ND particle in NCD-D, of which the size L_{fid} could be determined based on an independent and reliable information. For this, we found that the Raman frequency ω of 1925 cm^{-1} appears simultaneously for NCD-U4 with 6.30 nm listed in Table 2 and in NCD-D excited by 633nm laser (= 1.958 eV) listed in Table 2. It is thus reasonable to determine the particle selected by 633nm laser being the fiducial ND with $L_{\text{fid}} = 6.30 \text{ nm}$. Thirdly, after getting the difference of a certain excited energy relative to 1.958 eV, E_{dif} , the size of this excited particle is determined to be $L_{\text{se}} = L_{\text{fid}} + (G \times E_{\text{dif}})$. Moreover, we made ΔL_{se} to be $0.1 \times L_{\text{se}}$, as L is selected by RSSE. L_{ex} , ΔL_{se} , $(\Delta L/L)_{\text{se}}$ and q_r of NCD particles in NCD-D were listed in Table 2. From Table 2, it can be seen that two Raman peaks appeared in the fitted spectra exhibit same characteristics with those in samples NCD-U, meaning that the two peaks appeared in samples NCD-D must have the same properties of NCD-U.

The dependence of ω_L on q_r listed in Table 2 were plotted in Figure 3 (b) from which we can see that with increasing of q_r from the center of Brillouin zone the value of ω_L decreases from 1931.4 cm^{-1} to the smallest value of 1925.0 cm^{-1} and then increases to the largest value of 1335.0 cm^{-1} . That again indicates the appearing of downward bending feature. Since the largest value of 1335.0 cm^{-1} surpasses that at the center of Brillouin zone, 1332 cm^{-1} , the overbending feature observed in INS^{2,3} and IXS^{4,5} appears too. Therefore, the reliability of the LO PDR by RS shown in Fig 3 (a) obtains a further approval.

It is well known that a stronger test of the validity of a new procedure must show that the feature appearing in the new procedure, such as downward bending here, should also appear in traditional approaches. For this kind of checking, we quote a diamond PDR measured by a high-resolution IXS². This PDR has some specialties for comparing with the PDR measured by RS. First, it is from the highest resolution IXS measurement, as far as we know. Secondly, the authors of Ref 2 mentioned that the observed PDR is only along one direction of Δ , meaning that it is a good sample to

compare with the RS measured PDR with only one average direction of q . Thirdly, the PDR shown in Fig 3 of Ref 2 has a highest resolution in IXS and INS measurements. Based on the third specialty we have easily figured out that the measured frequencies ω at $q_r=0.0, 0.1$ and 0.2 are 1332 cm^{-1} , 1325 cm^{-1} and 1335 cm^{-1} , respectively. That shows in fact that there is also a downward bending feature before the appearing of the overbending. Especially, the smallest ω_L in the downward bending is 1325 cm^{-1} at $q_r = 0.1$, being basically equivalent to 1325.4 cm^{-1} at $q_r = 0.0834$ in the PDR measured for the NCD-U samples and 1325.0 cm^{-1} at $q_r = 0.0901$ in the PDR measured for the NCD-D sample. Obviously, those mentioned above gives the new RS approach a conclusive confirmation.

4. Conclusions

We propose a non-traditional approach by using Raman scattering (RS) of nanostructures with different sizes to measure the phonon dispersion relation (PDR). By using this new technique we measured the PDR of diamond in the reduced wavevector range q_r of 0.0 - 0.2 . Thanks to the high resolution in frequency and wavevector of phonons in the measurement of RS, the PDR deduced by different RS experiments for different kinds of nano-crystalline diamond samples are all showing a downward bending feature just away from the center of Brillouin zone, which was not observed before. In fact, the downward bending feature is also found in the PDR of diamond deduced by highest resolution inelastic X-ray scattering. Obviously all of the above facts prove the solid reliability of the new approach and the new-observed downward bending feature.

Moreover, the downward bending feature may give us a clue in deep understanding of the interactions presented in diamond, as the universally accepted overbending feature in the diamond PDR has been attributed to the strong effective second nearest-neighbor forces neglected before.

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Fig. 1. TEM images of nano-crystalline diamond samples of NCD-U1 (a), NCD-U2 (b), NCD-U3 (c), NCD-U4 (d), NCD-U5 (e), NCD-U6 (f) and SEM image of NCD-D (g).

Fig. 2. The observed (in solid line) and fitted (in dashed line) Raman scattering (RS) spectra excited by 514.5 nm laser for size-uniformed nano-crystalline diamond samples NCD-U (a) and excited by 325, 488, 515, 633, 785 and 1064 nm lasers for size-distributed NCD-U sample (b). The photo-luminescence (PL) spectrum of NCD-U are shown in (c). Where LO , TO , and D refer to the longitudinal optical, transverse optical and disorder structure phonons, respectively.

Fig. 3. The dependence of Raman frequencies of LO phonon ω_L with reduced wavevector q_r shown in (a) for nano-crystalline diamond (NCD) samples with size-uniformed NCD-U (drawn with black solid square) and with single particle NCD-S (drawn with red solid square) and in (b) for size-distributed sample NCD-D (drawn with solid triangle).

Table 1

The measured Raman frequencies ω excited by exiting wavelength $\lambda_{\text{ex}} = 514.5$ nm laser for nano-crystalline diamond (NCD) with uniformed size NCD-U. *LO*, *TO* and *D* label longitudinal optical, transverse optical and disorder phonons, respectively. L_{av} , ΔL_{av} and $\Delta L_{\text{av}}/L_{\text{av}}$ label the size, standard deviation and relative standard deviation, respectively. q_r is the reduced wavevector of q ($= q/q_{\text{max}}$; $q_{\text{max}} = \pi/a$, $a = 0.35668$ nm is the lattice constant of diamond).

Sample		NCD-U1	NCD-S1	UCD-S2	NCD-U2	NCD-U3	NCD-U4	NCD-U5
Size	L_{av} (nm)	581.6	90	35	6.61	6.30	5.55	3.95
	ΔL_{av} (nm)	52.7	~9,0	~3.5	0.75	0.68	0.54	0.40
	$(\Delta L/L)_{\text{av}}$	0.09	~0.10	~0.10	0.11	0.11	0.10	0.10
Raman frequency (cm ⁻¹)	ω_{LO}	1332.5	1329	1325	1324.3	1325.0	1326.3	1330.0
	ω_{TO}	/	/	/	1309.6	1310.1	1311.2	1313.7
	ω_{LO-TO}	/	/	/	14.7	14.9	15.1	16.3
	ω_D	1359.0	/	/	/	/	/	/
	q_r	0.00176	0.00630	0.0162	0.0756	0.0834	0.105	0.142

Table 2

The measured Raman frequencies ω excited by exiting wavelength by exiting wavelength $\lambda_{\text{ex}} = 325, 488, 515, 633, 785$ and 1064 nm lasers for size-distributed sample NCD-D. *LO* and *TO* label longitudinal optical and transverse optical phonons, respectively. L_{se} , ΔL_{se} and $\Delta L_{\text{se}}/L_{\text{se}}$ label the size, standard deviation and relative standard deviation. q_r is the reduced wavevector of q ($= q/q_{\text{max}}$; $q_{\text{max}} = \pi/a$, $a = 0.35668$ nm is the lattice constant of diamond).

Excited wavelength	λ_{ex} (nm)	1024	785	633	515	488	325
	λ_{ex} (eV)	1.211	1.580	1.959	2.405	2.538	3.815
Raman frequency (cm ⁻¹)	ω_{LO}	1331.4	1328.2	1325.4	1329.8	1330.1	1335.5
	ω_{TO}	/	1326.2	1323.2	1327.5	1327.6	1331.6
	ω_{LO-TO}	/	2.0	2.2	2.3	2.5	3.9
Size	L_{se} (nm)	7.464	6.890	6.30	5.906	5.399	3.412
	ΔL_{se} (nm)	0.746	0.689	0.630	0.591	0.540	0.341
	$(\Delta L/L)_{\text{se}}$	0.10	0.10	0.10	0.10	0.10	0.10
q_r		0.0761	0.0824	0.0901	0.0961	0.105	0.166

Tables

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fig1

fig2(a)

(a)

fig2(b)

(b)

fig2(c)

fig3(a)

fig3(b)